APPLICABILITY OF THERMOGRAVIMETRIC[+]
ANALYSIS TO SPACE CONTAMINATION

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1.0 INTRODUCTION

Contamination source kinetics is far from the stage of simply stating a few general laws to explain the entire process. However, there are common aspects in all source outgassing that lend to general classification and semiquantitative interpretation. Many investigators have measured outgassing rates of nonmetallic materials and have devised equations to approximate the rates at other temperatures and time durations other than those tested.[1,2] The spacecraft materials screening test[3] measuring the Total Mass Loss (TML) and the Collected Volatile Condensible Materials (CVCM) has become a standard method (ASTM E595) to quantitatively measure the outgassing of materials and their condensables in a vacuum environment. While this is an appropriate screening procedure to categorize materials, it does not provide enough source rate kinetic parameters to assess detail contamination problems. The need for higher temperature data resulting from laser radiation impingement has reinforced the need for a test method to obtain source parameters over a wide temperature range. Isothermal thermogravimetry, as a test method, appears to be too time costly taking from at least several days to several weeks. Dynamic thermogravimetry provides all the needed parameters within a few hours and appears to be a valid test technique.

Current contamination modeling theory has postulated applying kinetic rate theory to predict source outgassing characteristics. Once the source parameters are known, source rates are combined with mass transport equations, deposition rates, and finally reemission rates to assess the degree of deposition that will degrade spacecraft surfaces. The nature of the kinetic process is of the form

$$-\frac{dz}{dt} = \Theta \, f(z) \tag{1}$$

where Θ = the empirical rate constant and
$f(z)$ = a specific form which depends on reaction order, geometry of the sample and holder, heating rate, etc.
Applying this directly to polymeric source kinetics, results in the following expression for mass loss rate

[1]J.J. Scialdone, NASA TN D-8294, August 1976.

[2]T.M. Heslin, NASA TN D-8471, May 1977.

[3]R.F. Miraca and J.S. Whittick, Stanford Research Institute N67 40270, September 1967.

$$\dot{m}_s(t,T) = -k_s(T)m_s^n \tag{2}$$

where $\dot{m}_s$ = mass loss rate,

$k_s(T)$ = rate constant,

m_s = active mass remaining in the source, and

n = order of reaction.

The rate constant can be related to the temperature using the Arrhenius equation given by

$$k_s(T) = Ae^{-E/(RT)} \tag{3}$$

where A = frequency factor (independent of temperature),

E = activation energy of the process,

R = molar gas constant, 1.986 cal·mole^{-1}·K^{-1}, and

T = absolute temperature, K.

In general, a low activation energy means a reaction whose rate is only slightly affected by changing temperature and a high E means a large change with temperature. Most nonmetallic spacecraft materials exhibit a mass loss characteristic of a first order reaction. The mass loss rate is dependent on the first power of the mass remaining that is available for outgassing. The volatile mass remaining at any temperature can be determined by raising the temperature high enough to exhaust all of the volatile component and taking the difference in mass. Thus

$$k_s(T) = \frac{\dot{x}}{(a_o - x)} \tag{4}$$

where $\dot{x}$ = mass loss rate at temperature T,

a_o = total mass available for outgassing, and

x = mass loss at temperature T.

Notice that the quantity $(a_o - x)$ is the active mass remaining, m_s, of equation (2).

2.0 DYNAMIC THERMOGRAVIMETRY

Dynamic thermogravimetry is a continuous process that involves the measurement of sample weight as the temperature is increased by means of a programmed rate of heating. The output from a typical thermogravimetric analyzer consists of weight loss (TGA), expanded TGA (ten times), derviative of TGA (DTG), temperature, test chamber pressure, and residual gas analysis (RGA). The derivative thermogravimetry transforms electronically the weight data into a rate of weight change. Figure 1 shows a typical thermogravimetric data output for RTV-566 silicone adhesive. For our Mettler I system, in the dynamic mode, the temperature rate can be set
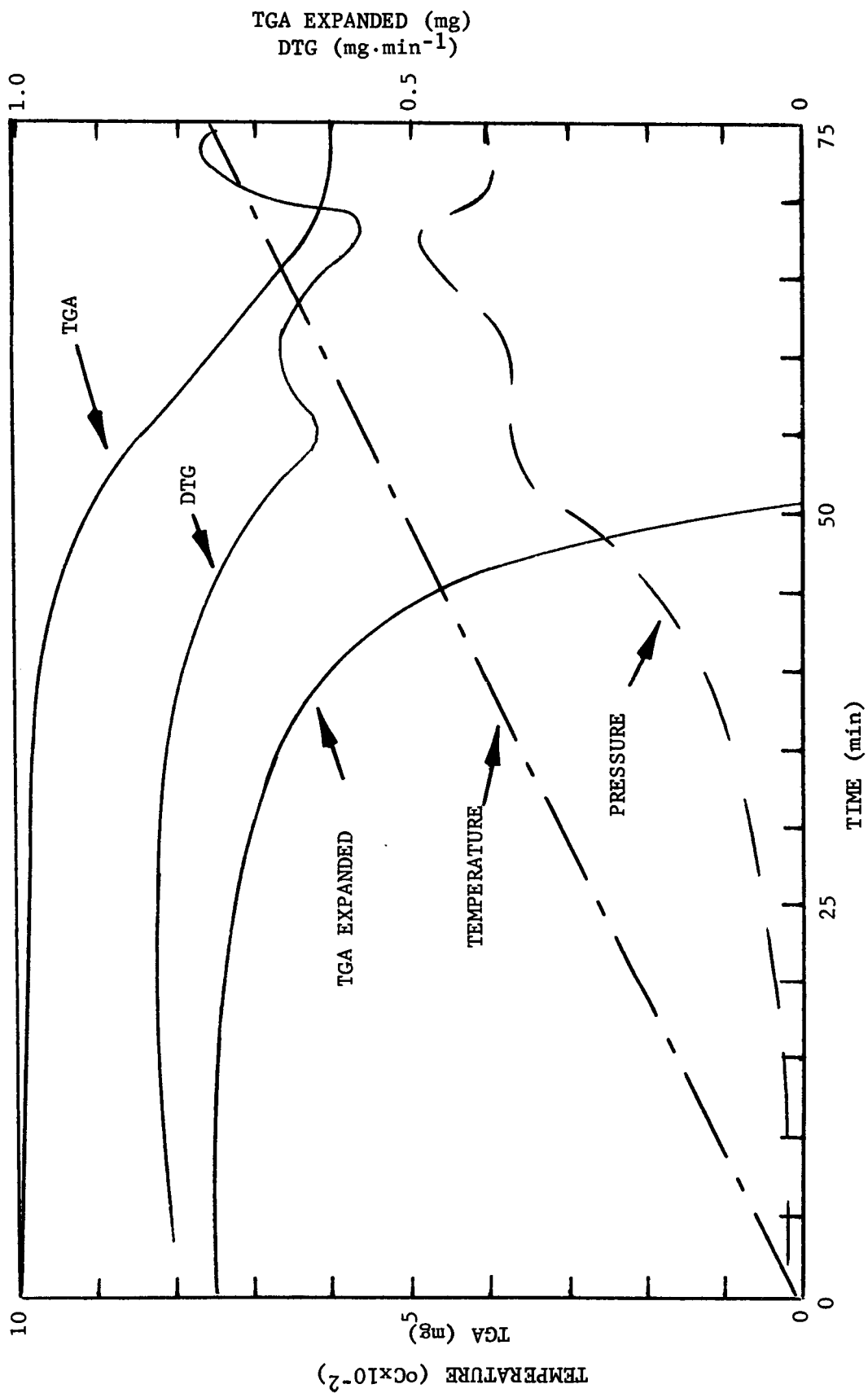
TGA EXPANDED (mg)
DTG (mg·min⁻¹)

Figure 1 Thermogravimetric Data Output For RTV-566

Figure 1 Thermogravimetric Data Output For RTV-566

from $0.2^{\circ}C \cdot min^{-1}$ to $25^{\circ}C \cdot min^{-1}$, at $\pm 4^{\circ}C$. The DTG data can be read to 0.01 mg·min^{-1}. In the dynamic mode to insure uniform heating of the entire sample, small amounts are used, normally 10 mg. Weight losses from 0 to 1g can be measured. In the zero to 10 mg range; the precision is ± 0.015 mg, the accuracy is ± 0.03 mg, and the readability is 0.005 mg. Temperatures from $25^{\circ}C$ to $1600^{\circ}C$ can be obtained; regulated to $\pm 1.5^{\circ}C$ and readable to $1.25^{\circ}C$. The temperature ramp in Figure 1 shows the $10^{\circ}C$ per minute heating of the sample from room temperature to over $700^{\circ}C$. The TGA curve shows the change in weight of the sample from just under 10 mg to 6.1 mg. The expanded TGA output continues throughout the full temperature range but was omitted to avoid a crowded figure. The presence of two maxima in the DTG curve indicates two components which outgas at different rates.

3.0 DYNAMIC THERMOGRAVIMETRY RESULTS

A systematic study of the TG parameters is currently in progress; however, numerous tests have been performed which illustrate the applicability of the technique to space contamination. Table 1 presents a summary of the TG tests performed, assuming all first order reactions. The column labeled T_{max} shows the maximum temperature reached by that specific test. The activation energy and the frequency constant were both obtained by a least square straight line fit from the plot of lnk versus T^{-1}. The correlation coefficient, r, near unity shows the linear curve does fit the data, strengthening our first order reaction assumption.

The first series of tests were on Dow Corning (DC) Silicone 92-007 white thermal control paint. All of the samples of DC 92-007 were from the same can of paint. The first two samples were obtained by painting the internal surface (a conic section) of the TG crucible liner. The density of the paint (1.19 g·cm^{-3}) and the area of the liner (1.01 cm^2) were used to estimate the thickness of the paint, 55 nm, 147 nm, and 325 nm. Another sample was obtained by scraping off a painted surface and dicing the scrapings into small pieces.

The analysis of the developed values for the rate constants showed that the mass loss rates were orders of magnitude too low to explain typical past spacecraft contamination problems. What seemed to be missing was a high volatile low temperature component. The small initial sample weights (6 to 17 mg) and the basic sensitivity of the TG prevented the detection of any small percentage components. The DC 92-007 material was painted on a clean glass surface and a large sample (657 mg) was peeled off, rolled, and placed into the TG crucible. The detection of two low temperature (weight loss 0.6% and 1.0%) components is shown in Table 1. Another large sample of DC 92-007 (583 mg) was tested by filling the TG chamber with nitrogen gas and cooling the paint sample down to $5^{\circ}C$ before starting to evacuate the chamber. No additional components were found.

Also shown in Table 1 is the TG data output for flight configured Ag/FEP thermal control surfaces, RTV-566 adhesive, and Astroquartz. The Ag/FEP sources consist of a film which is 20 to 40 nm of inconel, 100 nm of Ag, and 0.0508 mm of FEP as the outside surface. The RTV-566 was painted on a metallic surface and peeled off. The Astroquartz sample was silica fabric bonded to aluminum foil by FEP. Table 2 shows the prominant residual gas analyzer mass peaks at selected temperatures for RTV-566.

110

TABLE 1 SUMMARY OF TGA TESTS

SAMPLE	CONFIGURATION	CURE	AREA (cm^2)	INITIAL WEIGHT (mg)	ACTIVE WEIGHT (mg)	WEIGHT LOSS (%)	T_M (°K)	E (Kcal·Mole^{-1})	A (min^{-1})	r
DC 92-007-1	Painted Liner Thickness 55 nm	48 Hours Room Temp. 48 Hours 124°C	1.01	6.25	2.88	46.1	764	40.4	1.2×10^{11}	0.997
DC 92-007-2	Painted Liner Thickness 147 nm	48 Hours Room Temp. 48 Hours 124°C	1.01	16.78	8.76	52.2	765	51.1	1.7×10^{14}	0.997
DC 92-007-3	Diced DC A-4094	48 Hours Room Temp. 48 Hours 124°C	--	9.01	4.05	45.0	780	31.1	1.3×10^{8}	0.999
DC 92-007-4	Diced	48 Hours Room Temp. 48 Hours 124°C	--	9.72	4.42	45.5	788	52.8	1.8×10^{14}	0.996
DC 92-007-5	Rolled Strip 3.05 x 12.7 cm 0.143 mm Thick	None	77.4	656.7	3.94 / 8.54	0.6 / 1.3	394 / 487	15.9 / 13.4	4.1×10^{8} / 3.0×10^{5}	0.998 / 0.998
DC 92-007-6	Rolled Strip 3.05 x 12.7 cm	Cooled Sample In N_2 Atm to 5°C then Evacuated	77.4	582.77	4.68 / 5.83	0.8 / 1.0	387 / 477	19.0 / 6.5	5.5×10^{10} / 163	0.996 / 0.994
DC 92-007-8	Painted Liner Thickness 324 nm		1.01	36.98	0.33 / 8.14	0.9 / 22.0	430 / 788	6.5 / 52.4	156 / 1.2×10^{14}	0.994 / 0.999
DC 92-007-9	Painted Liner Thickness 325 nm		1.01	37.18	0.63 / 19.74	1.7 / 53.1	433 / 790	7.8 / 56.2	407 / 1.9×10^{15}	0.999 / 0.933
Ag-FEP-2	Diced 100 nm Ag 0.0508 nm FEP 20-40 nm Inconel 0.0508 3M-467	24 Hours 23°C & 45% R.H.	--	9.65	3.29 / 2.62 / 3.22	34.0 / 27.0 / 33.0	665 / 809 / 876			
Ag-FEP-3	0.4 cm Squares 100 nm Ag 0.0508 nm FEP 20-40 nm Inconel	24 Hours 24°C & 45% R.H.	--	9.89	2.58 / 6.94	26.1 / 70.2	816 / 901	71.4 / 92.1	7.3×10^{18} / 2.0×10^{22}	0.998 / 0.996
Ag-FEP-4	Rolled Strip Ag/FEP/Inconel	24 Hours 24°C & 45% R.H.	--	1644.64	0.47	0.028	523	8.0	382	0.9998
RTV-566-2	Peeled from Disc	Over 7 Days Room Temp.	--	10.08	3.29 / 0.72	33.0 / 7.0	836 / 966	28.5 / 56.3	4.9×10^{6} / 1.8×10^{12}	0.999 / 0.998
RTV-566-3	Peeled from Disc	Over 7 Days Room Temp.	--	500.69	7.01	1.4	487	21.3	2.3×10^{9}	0.997
RTV-566-8	Peeled and Diced		--	191.7	0.36 / 0.35	0.19 / 0.18	373 / 473	15.1 / 14.9	2.7×10^{8} / 2.1×10^{8}	
RTV-566-9	Peeled and Diced			8.29	1.72 / 1.38	20.8 / 16.7	843 / 963	34.2 / 78.5	1.23×10^{8} / 3.70×10^{17}	
Astroquartz	Diced Silica Fabric Bonded to FEP	None	--	11.39	0.52 / 1.11	4.6 / 9.7	808 / 879	73.8 / 909	9.0×10^{17} / 1.3×10^{21}	

Table 2 Residual Gas Analysis For RTV-566 Showing Major Peak Mass Number And Relative Peak Intensity At Selected Temperatures From 298 K to 1048 K

m/e	BKGD	298 K	398 K	873 K	959 K	1048 K
12				352	844	2494
13					1298	1168
14		618	509	1743	4014	3568
15		883	717	5808	15260	12544
16		9801	7633	8783	19853	25448
17		19561	15287	11293	13410	21278
18	284	36180	27513	18668	20205	33169
25				435	1003	1070
26				2698	5322	5844
27				1930	5354	8667
28	739	7390	6686	11725	18034	44937
29				1378	4637	5845
31					1512	
32		1350	1134	799	936	
36						2668
37						1110
38						2255
39					2671	7430
40	102	613	592	693	2262	3501
41				1098	4803	12692
42				787	2952	4810
43				797	8371	6769
44		564	551	1282	4099	17185

m/e	873 K	959 K	1048 K
45	1802	8198	3317
50		1250	1602
53		1323	
55		3682	7636
56		2586	7072
57		2757	4039
59	1497	7894	
66		1152	1077
67			3754
69		1450	4181
70		1651	1424
73	15724	52795	
74	1465	4611	
75	1879	4138	
76			2910
78	1167		
83			1398
84			1462
96	8066	4437	
103	1327	1270	2945
119	1502	1109	

m/e	873 K	959 K	1048 K
133	5429	4991	
147	1910	9017	
148		1495	
177	1653	2323	
191	3923	2117	
193	2251		
208	33786	16792	998
209	6744	3322	
210	4537	2108	

Table 3 presents the best estimate of the source kinetics parameters for the four sources tested, assuming first order reactions.

Table 3   Best Estimates For Source Kinetic Parameters Using Dynamic TG

MATERIAL	E (kcal·mole^{-1})	A (s^{-1})	WEIGHT LOSS (%)
DC 92-007	17.5	4.6×10^8	0.7
	6.9	4.0	1.2
	52.1	2.6×10^{12}	48.9
Ag/FEP	8.0	6.4	0.028
	71.4	1.2×10^{17}	26.1
	92.1	3.3×10^{20}	70.2
RTV-566	21.3	3.8×10^7	1.4
	28.5	8.2×10^4	32.6
	56.3	3.0×10^{10}	7.9
Silica/FEP/Al	73.8	9.0×10^{17}	4.6
	90.0	1.3×10^{21}	9.7

4.0 ISOTHERMAL THERMOGRAVIMETRY

The Mettler 1 TG instrument had been used previously to perform iso-thermal TG tests on Dow Corning Silicone 6-1106, Viton A, Shell Epon 828 epoxy, Choseal silicone, and glass-filled diallyl phthalate.[5] These tests have shown that TGA can accurately predict isothermal kinetics at some 500°C lower temperatures than observed during dynamic TG testing. For the low out-gassing materials, a single isothermal run would take up to 30 days to complete. For these tests the high volatile component was not isolated.

Isothermal mass loss for DC 92-007 and RTV-566 were recently meas-ured. A 2.54 cm diameter disc painted with primer DC A-4094 and DC 92-007 was heated to 115°C and held at that temperature. However, the outgassing rate for this sample (initial weight 44.31 mg) was too low to be detected. The temperature was then elevated to 293°C. Integrating equation (2) to obtain the time dependent form of the mass loss rate and then differen-tiating the result gives

$$\dot{m}_s = a_o k e^{-kt}. \tag{5}$$

[5]H.A. Papazian, J.Appl. Polym. Sci., 16, 2503 (1972).

Plotting $\ln \dot{m}_s$ versus t and using a least square linear fit gives a value of $k = 5.93 \times 10^{-4}$ min^{-1} for $T = 566$ K, $a_o = 44.2\%$, and a correlation coefficient of $r = 0.7276$. Using the kinetic parameters for DC 92-007 from Table 2 allows a comparison between dynamic and isothermal TGA; Figure 2 presents a plot of $\ln \dot{m}_s$ versus t for these two methods. The values are quite close considering that the dynamic parameters are for the paint only and do not include the primer, DC A-4094.

The very low outgassing rate of RTV-566 led to performing the isothermal test using a 61.07 mg sample diced up to release the full active components. The RTV-566 was heated to 125°C for 5451 min (90.85 hrs). The mass loss rate was too low for the DTG sensitivity and the rate was determined from the slope of the expanded TGA output. Table 4 presents the test results and the calculated values using the dynamic parameters for RTV-566 from Table 3.

Table 4   RTV-566 Isothermal   Mass Loss Rates At 125°C And Mass Loss Rates Using Dynamic TG Parameters

TIME	ISOTHERMAL MASS LOSS RATE	TGA DERIVED MASS LOSS RATES EACH COMPONENT		
(min)	$(mg \cdot min^{-1})$	$(mg \cdot min^{-1})$	$(mg \cdot min^{-1})$	$(mg \cdot min^{-1})$
1626	2.6×10^{-5}	2.49×10^{-6}	2.15×10^{-8}	1.01×10^{-18}
2586	5.7×10^{-5}	3.26×10^{-8}	2.15×10^{-8}	0
3546	5.7×10^{-5}	4.29×10^{-10}	2.15×10^{-8}	0

As Table 4 shows, the dynamic TG derived mass loss rate is several orders of magnitude lower than the measured isothermal mass loss rate. The TML for this test for the first 24 hours is 0.49% which is much higher than the NASA Goddard values ranging from 0.14 to 0.25%. The difference could be explained by the fact that the samples tested were in flight configuration with a primer of SS-4155 as the undercoating. Thus, the dynamic TGA values can vary from the isothermal based on the amount of primer that is scraped off for each sample.

5.0   HIGHER ORDER REACTION THEORY

The first order reaction theory applied to TG used the method of Freeman and Carroll.[6] The method of Reich and co-workers[7] uses the position of the TGA inflection point to determine not only the rate constant, k, but the order of the reaction, n. Differentiating the general rate equation (2) with respect to T and setting the result equal to zero gives

$$n = (E/R) \frac{\dot{m}_M \dot{T}}{-\dot{m}_M T_M^2} \tag{5}$$

[6] E.S. Freeman and B. Carroll, J.Phys.Chem., 62, 394 (1958).

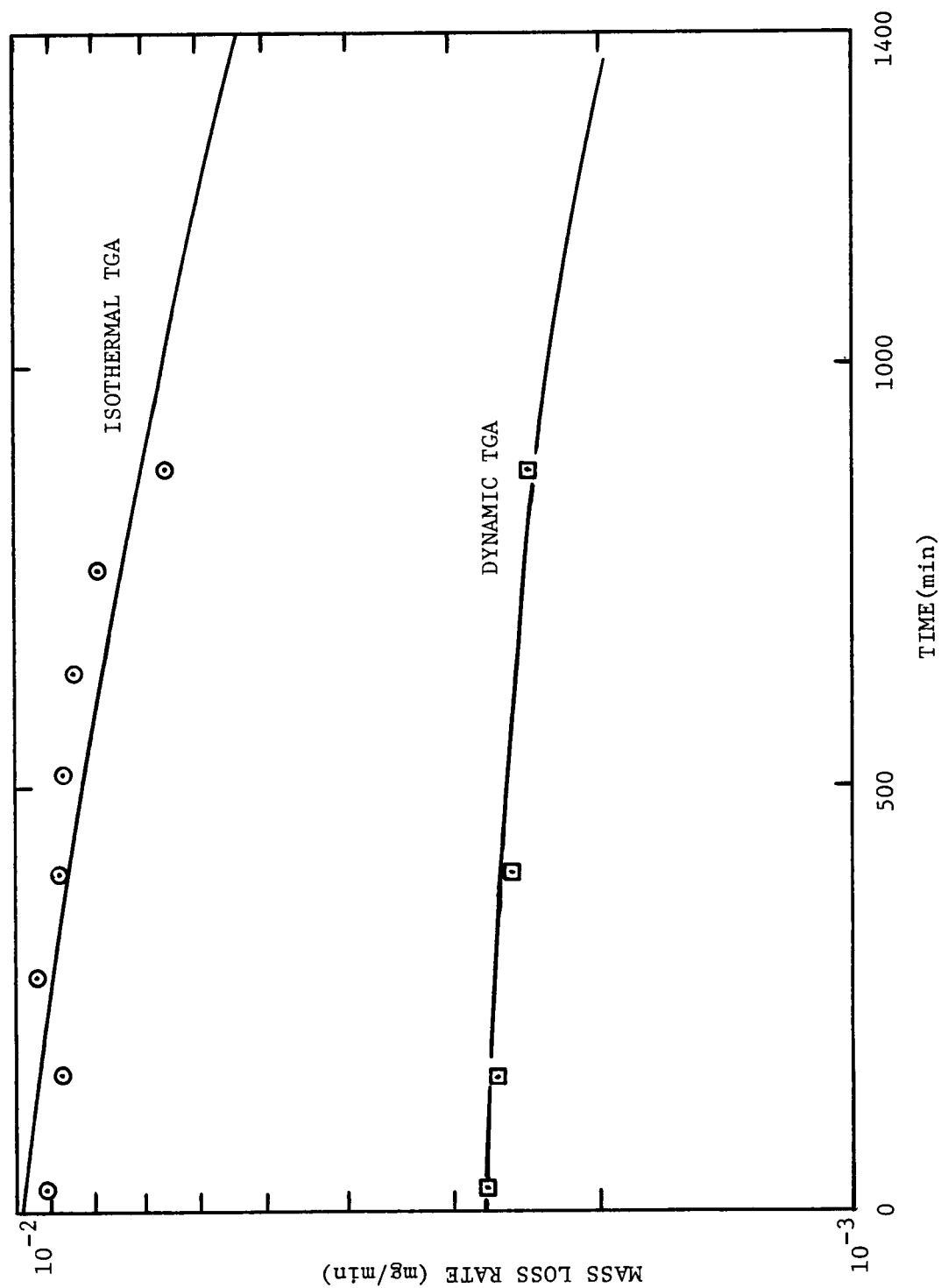[7] L. Reich, H.T. Lee and D.W. Levi, J.Polym.Sci., B1, 535 (1963).

Figure 2   Isothermal TGA Mass Loss Rate for DC 92-007 at 293°C with Comparison Curve Using Parameters Obtained from Dynamic TGA

where m_M = weight of active material remaining at inflection point,

$\dot{m}_M$ = DTG value at inflection point,

T_M = absolute temperature at inflection point, and

$\dot{T}$ = rate of heating.

Taking the logarithm of equation (2) and using equation (5) gives

$$\ln\,(-\dot{m}_s) = \ln A + (E/R) \left[\frac{m_M \dot{T} \ln m_s}{-\dot{m}_M T_M^2} - T^{-1} \right] \qquad (6)$$

Plotting the $\ln(-\dot{m}_s)$ versus the term in the bracket of equation (6) allows E to be determined from the slope and A from the intercept of the linear relation. Table 5 shows the result of applying this method to the DC 92-007 data. The large values of n seem to indicate the questionability of using this analysis method with our intrumentation. The low temperature components of DC 92-007 were especially difficult to analyze because of the small percent of weight loss (less than 2%) and that they occur where the required linear temperature increase is difficult to control.

Table 5   TG Data For DC 92-007 White Thermal Control Paint

SAMPLE NUMBER	m_M (mg)	$\dot{m}_M$ (mg·min^{-1})	T_M (K)	$\dot{T}$ (K·min^{-1})	n	E (Kcal·mole^{-1})	A (min^{-1})(g·cm^{-2})$^{1-n}$
1	1.03	0.350	768	10.0	1.15	46.0	5.4×10^{12}
2	3.73	1.302	766	10.0	1.54	62.5	1.5×10^{17}
4	2.60	0.675	788	10.0	2.55	81.8	5.6×10^{21}
5	2.04	0.860	398	18.4	2.51	18.1	1.2×10^{9}
	3.99	0.865	498	15.0	0.79	5.6	44.0
6	2.21	0.900	385	21.0	4.46	25.7	9.3×10^{12}
	4.80	1.075	477	16.6	0.78	4.7	53.0

6.0   PROBLEM AREAS

Several potential problem areas in dynamic TG have been observed. Standard TG procedures use a diced specimen, however applications of TGA to spacecraft surfaces requires mass loss per unit area. The few TG tests which were run with painted surfaces at various thicknesses (see Table 1) do not indicate any definite trend. Thick outgassing surfaces may require additional diffusion terms in the kinetic equations to adequately describe the release of mass.

Another potential problem is the extrapolation of dynamic TG parameters to low temperatures. Low temperature components may be very dependent on handling and the environment history of the sample material.

For spacecraft surfaces, temperatures are usually low and thus the solvent (this term encompasses highly volatile components, unreacted plasticizers, curing agents, etc.) may be the dominant weight loss component.

Estimation of a_o is difficult in most kinetic calculations. For reactions with a single component, a_o is the total weight loss. However, multi-steps in the basic sigmoidal TGA curve requires judgment in locating each portion of the weight loss participating in each step. There are several techniques proposed in TG literature reviewed, but none of which appears to have any better physical basis. Slight variations in a_o does not effect greatly the calculated value for E but it does vary A, the frequency constant.

Some of the advantages of dynamic TG over isothermal are as follows:

1. Short test time, about one hour compared to periods of at least 24 hours at each (at least three) different temperatures;

2. Significantly less data to process and analyze;

3. Continuous measurement of weight loss at each increment of temperature captures all kinetic features;

4. Single sample avoids variations due to source preparation; and

5. Fulfills need for screening materials at laser induced temperatures.

Some disadvantages of dynamic TG are:

1. Necessity of precise control of the temperature rate;

2. Low sensitivity for small percentage active components;

3. Difficulty in maintaining uniform temperature rate to detect low temperature components; and

4. Necessity that diffusion barriers be negligible.